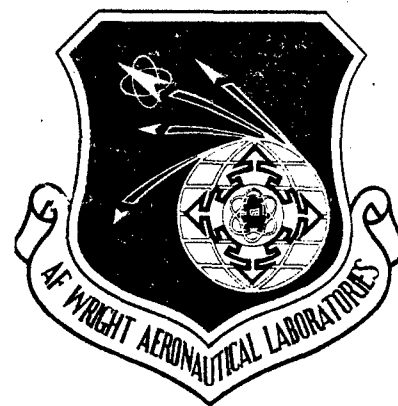


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INFLUENCE OF PROCESSING IN THE SOLID STATE  
MORPHOLOGY OF ABPBI/PBT POLYMERIC COMPOSITE  
FILMS: X RAY STUDIES



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November 1982

Special Interim Report for Period September 1980 - January 1981

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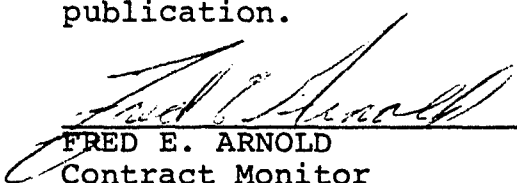
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FOR THE COMMANDER

  
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  X-ray diffraction patterns of ABPBI/PBT polyblend films suggest the formation of polymer-solvent complexes at the molecular level. This effect may be misinterpreted as a "new phase" formed as a result of blending the two polymers. Polymer-solvent complexes are crystalline and can be oriented by usual methods. The nature of the x-ray diagram of the polymer-solvent complex depends upon blend composition, type of solvent and the method employed for film processing (casting or quenching). Neutralizing or annealing of polyblend films (in		

20. order to eliminate the solvent) results in x-ray diffraction patterns which can be explained in terms of additive contributions from the constituent polymers. The ABPBI/PBT polyblend films thus have a two-phase morphology. Various methods for the processing of these novel polymer mixtures are presented and discussed in terms of their influence on the microstructure.

## FOREWORD

This report was prepared by the University of Dayton Research Institute, Nonmetallic Department, Polymer Group. This work was initiated under U.S. Air Force Contract #F33615-81-C-5019 New Polymeric Materials for Advanced Aerospace Vehicles. It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the contract monitor. Authors were Dr. A. K. Kulshreshtha, and Mr. G. E. Price, University of Dayton Research Institute with Dr. Donald R. Wiff the principal investigator.

This report covers research conducted from September 1980 to January 1981.

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## SECTION I

### INTRODUCTION

Continuing advances in aerospace missile and weapons technology as well as the rising energy costs have created an increasing demand for thermally-stable, lightweight polymeric materials. As a result of fundamental studies which C. S. Marvel started almost 30 years ago, there exists today several polymers which in their strength and modulus are comparable to many metals including soft steel. These high strength, high modulus (HSHM) polymers have a specific gravity of only 1.4 g/cc as compared with 7.5 g/cc for steel. As a consequence, their strength-to-weight ratio is substantially superior to that of steel. Examples of HSHM fibers are: Kevlar, Poly(p-Benzamide), and Poly(p-phenylene Benzobisthiazole). The latter polymer, abbreviated PBT, is the topic polymer of this investigation. PBT is a rod-like aromatic-heterocyclic polymer which has been processed into fibers and films having a high degree of crystallite orientation and modulus.<sup>1-6</sup>

In order to emphasize the uniqueness of blending a rigid rod-like polymer (PBT) with a somewhat flexible coil polymer (ABPBI), the "Molecular Composite Concept"<sup>7-9</sup> has emerged whose feasibility has been demonstrated.<sup>10</sup> The intent is to reinforce the coil-like or amorphous polymer with the rod-like polymer,

thus forming a composite on the molecular level, analogous to chopped fiber reinforced composites. PBT is an obvious choice for the rod-like component in view of its high molecular weight, high modulus and excellent thermal stability. ABPBI was chosen as the coil-like component because of the simplicity of its repeat unit, its flexibility, its believed compatibility to PBT because of similar molecular structure, and availability.

The objective of the present work is to examine the microstructure of the solid state of ABPBI/PBT polyblend films prepared with a common solvent. X-ray diffraction (XRD) techniques have been employed for this purpose. Since the polyblend films have been prepared from solution, x-ray diffraction was expected to provide answers to the questions:

- (i) Is there any residual solvent in the polyblend film?
- (ii) What is the nature of association between the polymers and the solvent?
- (iii) What is the morphology of the polyblend as it is processed and after solvent removal?
- (iv) What is the influence of the type of solvent employed upon the morphology of processed polyblend film?
- (v) Does solvent act as a plasticizer? If so, can it be used to crystallize the polyblend microstructure by means of high-temperature annealing?

The x-ray diffraction data on polyblends has been plotted as bar graphs showing various d-spacings observed in the x-ray pattern.

SECTION II  
INTERPRETATION OF X-RAY DATA  
, BASED ON BAR GRAPHS

It is very difficult to arrive at a definitive interpretation of x-ray data in view of the following limitations:

(1) The unit cells of rigid-chain polymer, PBT and the flexible chain polymer, ABPBI are not known precisely and unambiguously. This renders the assigning of hkl indices to various reflections on the bar graph impossible at this time.

(2) Cast films of polyblends in many situations show un-oriented x-ray diffraction patterns. Thus, it is difficult to decide whether a given reflection on the bar graph should be attributed to equatorial or meridional interferences.

(3) In blends of certain compositions, the x-ray contributions of both constituent polymers add-up, leading to a complexity of the interpretation task.

(4) Most polyblend films contain free solvent as well as solvent complexed with polymers.

(5) The physically-trapped solvent in blends makes its contribution to the x-ray scattering by giving a very broad, diffuse reflection which obscures the diffraction pattern.

(6) In most polyblends, x-ray bar graph data proves the existence of polymer-solvent adducts or polymer-solvent complexes which may be stoichiometric in nature. The nature of the x-ray diagram of this complex depends upon (a) the casting solvent (methane sulfonic acid, MSA; or fuming nitric acid FNA), (b) the blend composition of the film and (c) the amount of solvent present in the film.

(7) The x-ray diagrams of polyblend films; which already have contributions from constituent polymers, solvent (bound or unbound), and polymer-solvent complexes: are strongly influenced in all cases by the addition of methyl sulfoxide (DMSO).

(8) In some cases, the x-ray patterns of polyblends show an overall diffuseness and a lack of crystallinity. Some diffraction

lines are too diffuse to allow one to calculate an average d-spacing. Attempts to crystallize such films by heat-treating are defeated by a complete change of the x-ray diagram, caused by polymer-polymer phase separation and by a decomposition of polymer-solvent complex(es).

a) Polymer Solutions

In order to investigate the influence of the transition from solution to the solid state on blend morphology, experiments were undertaken on solutions of pure PBT and a 40/60 (ABPBI/PBT) polyblend:

Several problems were encountered in preparing the samples of solutions for the purpose of x-ray diffraction. The information contained in the x-ray diagrams was of limited utility, especially since the x-ray patterns were obtained using conventional x-ray generator which lacked sufficient x-ray intensity. Polymer solutions were sealed inside a thin glass capillary for mounting on a Statton x-ray camera. Due to the very high viscosity and gel-like nature of solutions, even at low solute concentrations, it was extremely tedious to pour the solution inside a 1-mm diameter capillary. Another complication to the experiments was the observation that once exposed to x-rays, the solutions tended to be "coagulated" during the exposure. This problem might have arisen due to high vacuum in the x-ray camera and ineffectiveness in sealing the capillary containing the solution.

The results of x-ray experiments on solutions of PBT and 40/60 polyblend of ABPBI and PBT are summarized. The main features common to the x-ray diagrams of solutions are: (a) a lack of preferred orientation, (b) very few, extremely broad diffraction lines, and (c) a tremendous amount of diffuse x-ray scattering. The PBT solutions depicted a very broad amorphous halo at low diffraction angles, which is represented as the very broad region (extending from 9.5Å to higher spacings in Figure 1). In the solution of the polyblend, the scattering in this region was weak and not so broad. At large angles (i.e., smaller d-spacing), another diffraction line was seen around 4.5Å d-spacing in all

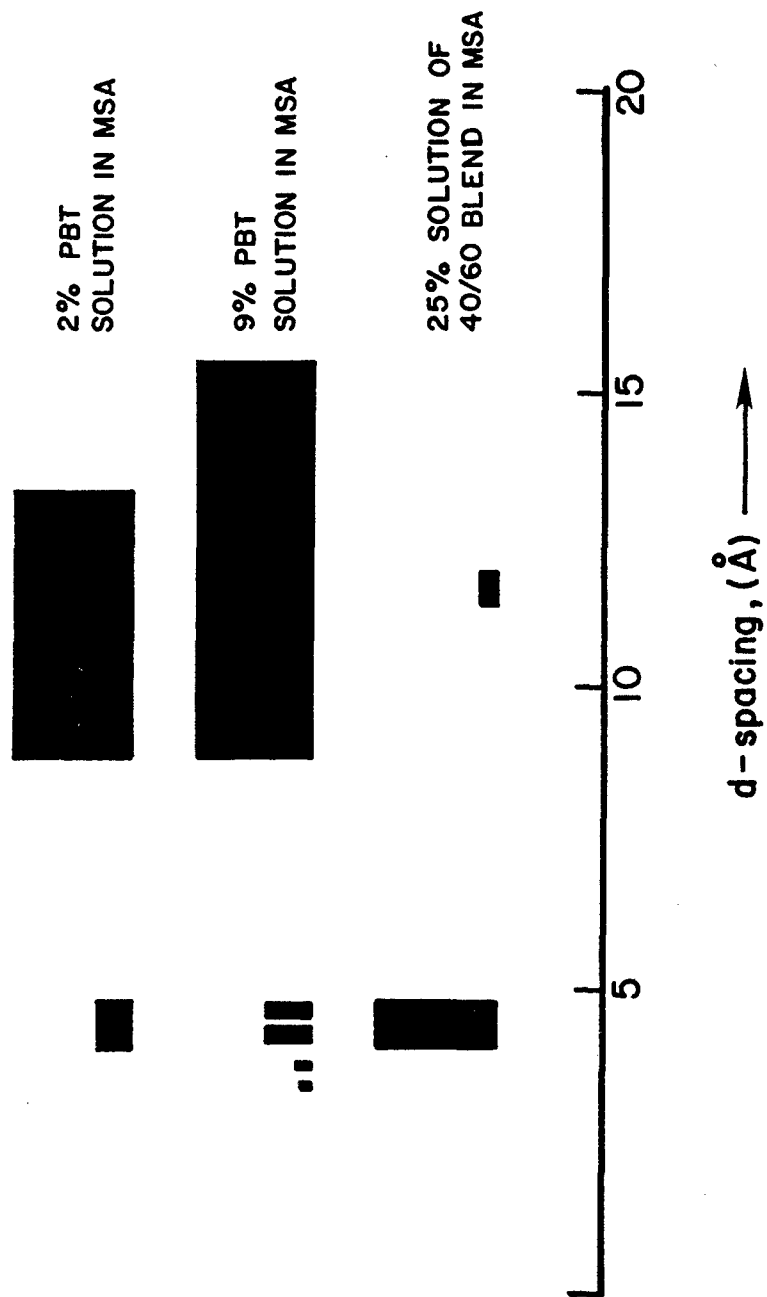


Figure 1. Comparison Between Various Diffraction Data for PBT Solutions.

the solutions. This spacing is attributed to scattering by the pure MSA solvent and it was verified in a control experiment that pure MSA solvent gave rise to a single d-spacing at 4.41Å.

The presence of neighboring lines (in 3-5Å range) in the x-ray pattern of 9% PBT solution is attributed to coagulation effects.

b) 40/60 Film Cast from MSA

It is necessary to understand the structure of the solid state of the as-cast film in relation to the structure of the constituent polymers. Since the as-cast film contains about 30% of solvent (MSA), x-ray diffraction technique can be employed to follow the structural changes resulting from a removal of the solvent.

Basically, there are two possible routes to removal of solvent from the cast polyblend. The first and simpler route is to neutralize the acid solvent with aqueous  $\text{NH}_4\text{OH}$ , followed by washing and drying. A shrinkage of the polyblend film has been observed to occur during this neutralizing process. The second route is to heat the film (in an inert gas atmosphere or under vacuum) until the solvent leaves the film. This route is thought to be more rewarding, as it offers the possibility of crystallizing the glassy, rod-like polymer (PBT), with solvent acting as a plasticizer during annealing. Thus, a transition from solution to the solid state is represented by the following sequence:

Solution of Two Polymers in MSA

As-Cast Film (With MSA).

Cast Film (Without MSA)

This transition from solution to solid state in 40/60 blend has been followed by the x-ray diffraction and the results are depicted as bar graphs in Figure 2.

With reference to Figure 2 the diffraction from a 25% solution of the two polymers was amorphous and showed two broad halves at about 4.4Å and 11.7Å. The x-ray pattern of the as-cast film was unoriented, Figure 3. The film could be mechanically

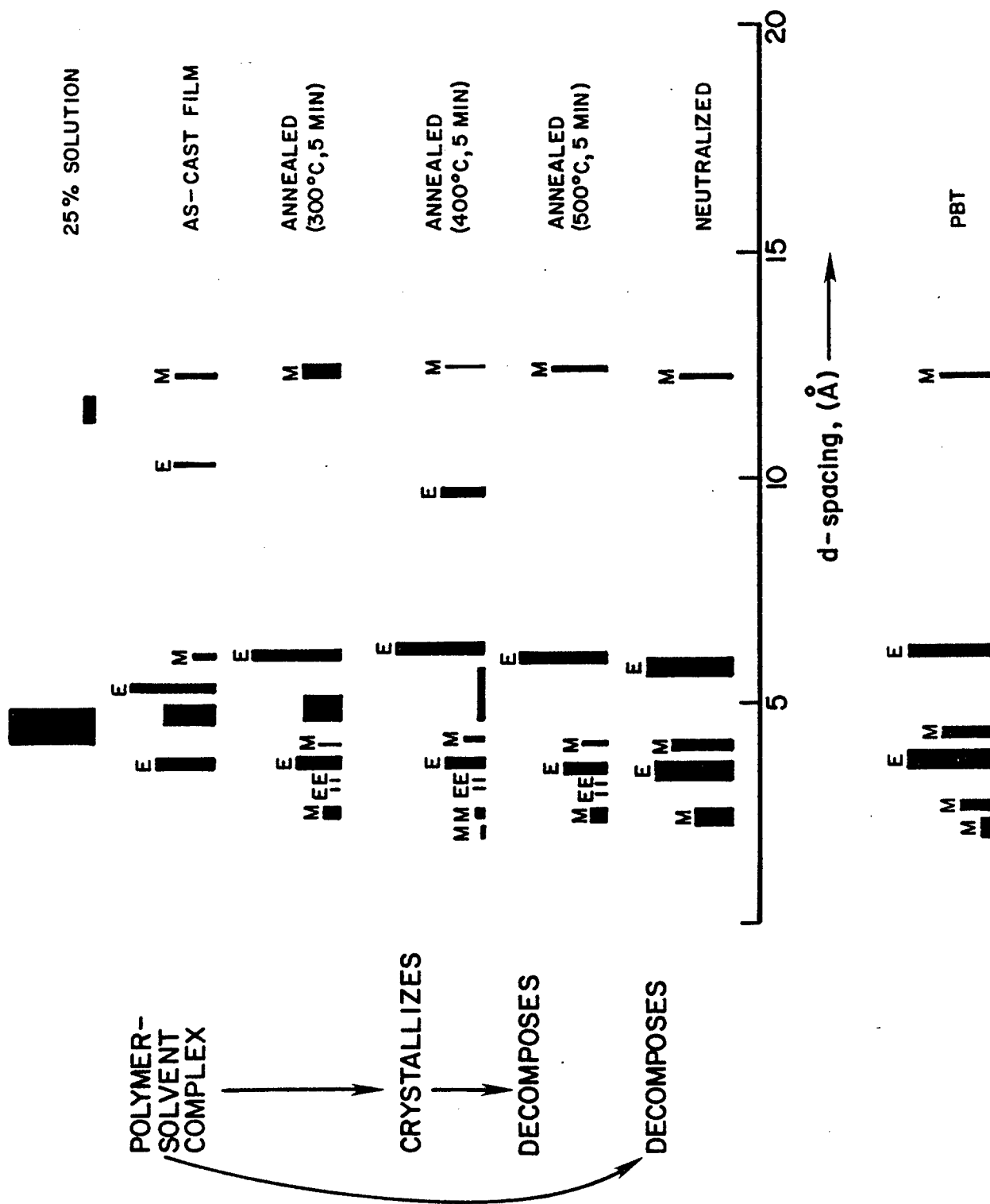


Figure 2. Comparison Between Various Diffraction Data  
Relating to 40/60 Films Cast from MSA.

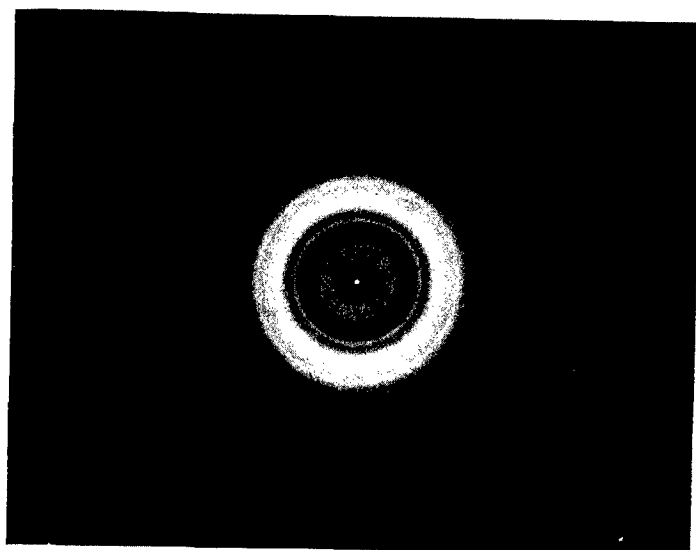


Figure 3. X-ray Photographs of MSA-cast Films (a) 80/20 Blend,  
(b) 40/60 Blend.



stretched just enough to discriminate between the equatorial and meridional interferences. This pattern has been interpreted as diffraction of x-rays by a polymer-solvent complex, formed by solvent molecules acting as "bridges" between two adjacent rod-like molecules. This polymer-solvent adduct or complex should exhibit a large spacing on the equator due to a lateral expansion of the lattice, but should not show any change in c-axis arising from periodic axial structure. Thus, the bar graph of Figure 2 shows an equatorial spacing of 10.4A corresponding to polymer-solvent adduct and an unchanged spacing of 12.4A on the meridian. The other observed spacings at 5.25A on equator and 6.1A on meridian can be explained as second-order reflections, showing halved d-spacings. This leaves only spacings at 3.5A and 4.7A to be accounted. Of these, the 3.5A equatorial spacing is universally observed in most aromatic-heterocyclic polymers containing benzene rings. The spacing at 4.7A is interpreted as arising from free or unbound MSA in the film, because this spacing vanishes from the pattern when solvent is removed from the film. It represents one of the two spacings observed in the x-ray pattern of polyblend in the solution form.

When the cast polyblend film was neutralized with  $\text{NH}_4\text{OH}$ , the polymer-solvent complex decomposes resulting in a shrinkage of lattice size (i.e., the unit cell volume). The resulting neutralized film showed a diffraction pattern which was indistinguishable from the diffraction pattern of pure PBT polymer (spun fibers or neutralized cast film of PBT). There were no diffraction lines corresponding to ABPBI in the pattern of 40:60 neutralized, cast film. The scattering by rod-like molecular aggregates thus dominated the x-ray pattern of neutralized polyblend.

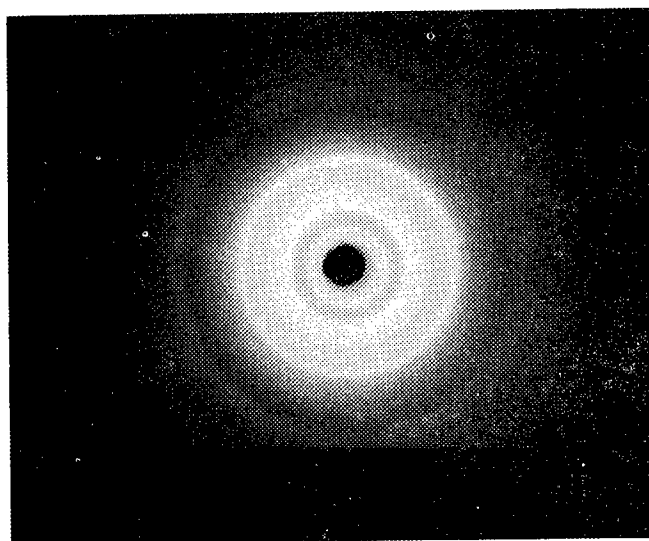
The as-cast film was annealed at 300°C, 400°C, and 500°C, in three different experiments to examine the process of decomposition of the polymer-solvent complex present in the as-cast film. Annealing of the as-cast polyblend at 300°C led to some crystallization in the x-ray pattern of the polymer solvent

complex, as indicated by an increase in the number of diffraction spacings on the bar graph (Figure 2). The spacing attributed to free solvent was shifted to 4.8A (toward higher spacing side) and was somewhat reduced in height. The equatorial spacing at 3.5A now had two neighboring spacings at 3A and 3.2A and this "equatorial triplet" appeared in all x-ray patterns of annealed, rod-like polymer (PBT). There is an anomaly, however, i.e., the 5.25A and 10.4A spacings attributed to the expanded unit cell was absent in this pattern. The emergence of the strong equatorial peak at 6A was an indication of decomposition of the initial polymer-solvent complex and crystallization occurring from an aggregation of rod-like molecules.

The x-ray pattern of as-cast film, annealed at 400°C is very crystalline (Figure 4) and shows an equatorial spacing at 9.6A (this finding has been checked by repeated experiments). The origin of this diffraction peak are not understood, but may be attributable to crystallization or to stoichiometric changes in polymer-solvent binding. The solvent spacing has shifted to even higher d-spacing of 5.1A and this reflection is extremely diffuse and weak in intensity. Finally, the x-ray pattern of as-cast film annealed at 500°C (Figure 5) does not show any peaks arising from the polymer-solvent complex or from free solvent. It simply represents diffraction by rods which have now aggregated and crystallized as a result of annealing. The difference between this pattern and the pattern of neutralized film are two equatorial lines at 3A and 3.2A which are a result of improved crystallinity due to annealing. Thus, no matter what route is taken to remove solvent from the as-cast film, the resultant film shows diffraction contributed only by pure PBT.

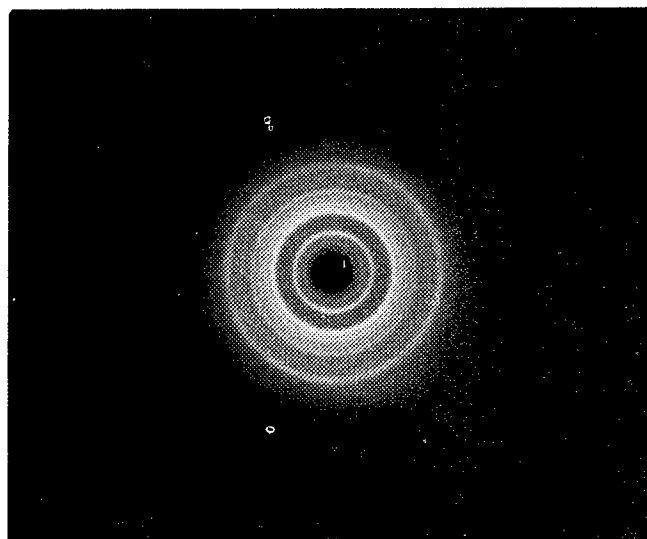
c) 80/20 Film Cast from MSA

If the polymers ABPBI and PBT are indeed compatible, they should form molecular alloys, especially in dilute blends. However, from a consideration of the polymer-polymer-solvent phase diagram it can be predicted that rod-coil phase separation must



40/60 MSA-CAST, ANNEALED  
AT 400°C

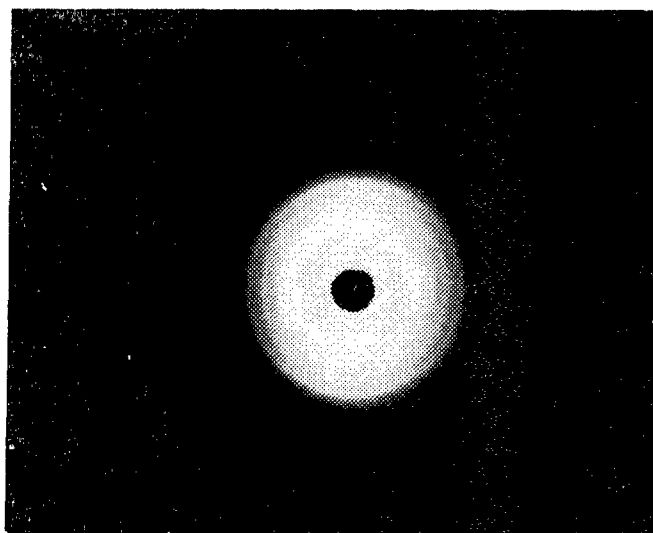
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40/60 MSA-CAST, ANNEALED  
AT 10000 LB., 425°C

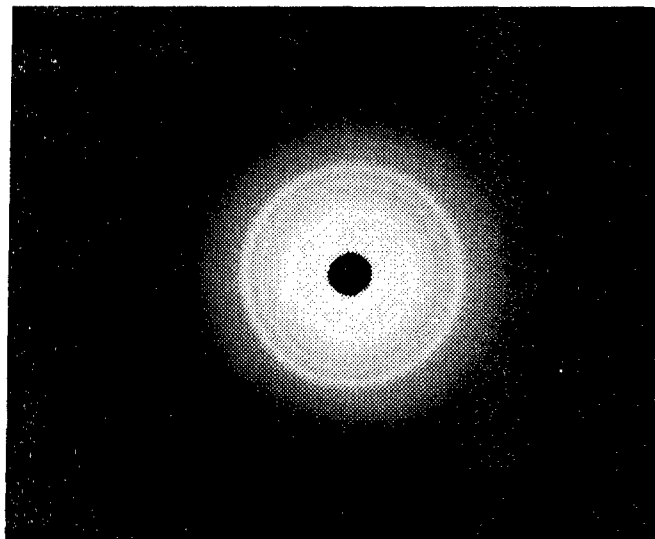
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Figure 4. X-ray Photographs of MSA-cast 40/60 Polyblend Film (a) Annealed at 400 C (b) Pressure-Annealed at 10000 lb., 425 C.



80/20 MSA-CAST, ANNEALED AT  
500°C FOR 5 MIN IN VACUUM

a



40/60 MSA-CAST, ANNEALED AT  
500°C FOR 5 MIN IN VACUUM

b

Figure 5. X-ray Photographs of MSA-cast Polyblend Films, Annealed at 500 C for 5 Min in Vacuum (a) 80/20 Blend (b) 40/60 Blend.

occur above a critical concentration (which is a function of blend composition, aspect ratio, etc.). In the process of casting films from a dilute solution, this critical concentration is always exceeded. Therefore, cast polyblend films must exhibit a two-phase morphology and indeed the morphological studies of ABPBI/PBT cast films by means of electron microscopy have established the phase-separation phenomenon.

Figure 6 shows the x-ray bar graphs of 80/20 polyblend film, as-cast and neutralized. For comparison, x-ray spacings of ABPBI cast film (neutralized) and PBT are shown as reference. In the as-cast film, the spacing of 9.9A corresponds to the expanded molecular lattice due to polymer-solvent complexation. The broad spacing at 4.8A is associated with the presence of solvent in the as-cast film. The spacings at 4.15A and 12.25A correspond to the meridional reflections arising from axial repeat in PBT. The reflection at 6A is equatorial in origin, arising from rod-like PBT molecules. The reflection at 3.8A may be the 003 meridional reflection from ABPBI matrix or may reflect a new spacing arising from polymer-solvent complex.

Neutralizing of the 80/20 cast polyblend film (Figure 17) results in a disappearance of 9.9A and 4.8A spacings (present in as-cast film) due to a breakdown of the polymer-solvent complex and solvent removal. All the d-spacings present in the bar graph of the neutralized 80/20 polyblend (Figure 6) can be accounted for by contributions from pure ABPBI and pure PBT materials. For instance, the 7.4A spacing is very close to the 7.3A spacing observed in pure ABPBI cast film (neutralized). The remaining spacings arise from pure PBT. The spacings at 3.5A and 6A in the neutralized polyblend correspond to equatorial spacings of PBT and 2.5A, 4.2A and 12.3A spacings correspond to meridional 005, 003, and 001 spacings of PBT. The x-ray pattern of neutralized 80/20 cast polyblend thus reflects phase-separation behavior in which only the additive contributions from different polymers (phases) are observed. The x-ray pattern does not indicate any evidence of polymer-polymer miscibility leading to the formation of a polymer alloy (or a third phase).

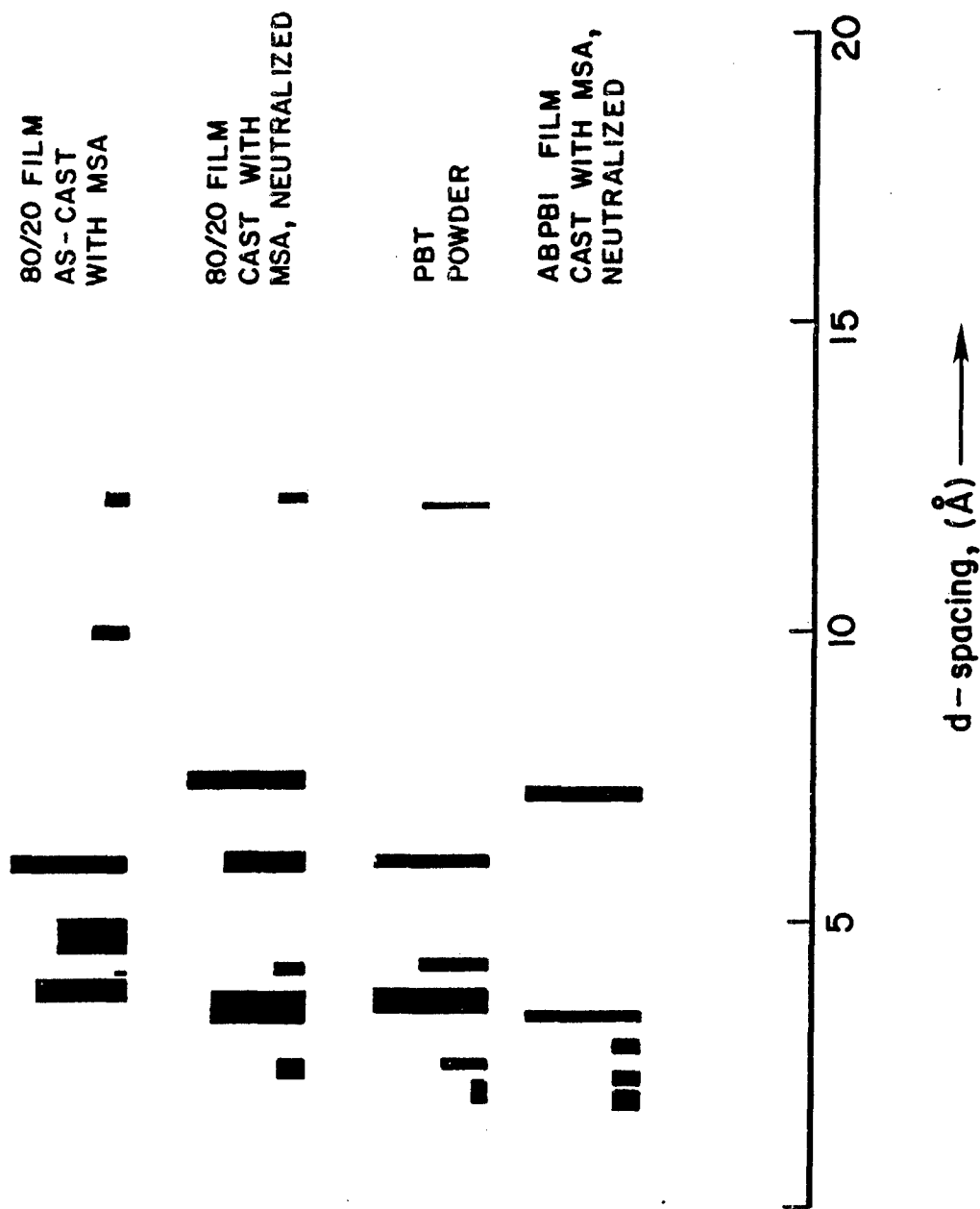


Figure 6. Comparison Between Various Diffraction Data Relating to 80/20 Films Cast from MSA.

d) Polymer-Solvent Complex

In the control experiments, the pure or "virgin" polymer (ABPBI or PBT) in a powder form was packed inside a quartz 1mm capillary. The x-ray diffraction from this powder was recorded on a flat film using the Statton Polymer Camera. Subsequently, a few drops of MSA were added to this powder inside the capillary until a sol/gel boundary was visible. X-ray diffraction pattern of this gel of polymer-solvent complex was then obtained.

Figure 7 shows the bar graphs of pure PBT powder, PBT-MSA complex, and finally of the pure PBT obtained by annealing of the PBT-MSA complex to eliminate the MSA. The x-ray bar graphs of initial PBT powder and annealed PBT powder are similar - the latter shows a general sharpening of x-ray lines and emergence of two new lines at 3A and 3.2A due to improvement in the crystallization of rod-like macromolecules by annealing. The x-ray bar graph of PBT-MSA complex, on the other hand, differs very considerably from the bar graphs of pure PBT, perhaps due to an expansion of lattice caused by complex formation. The x-ray pattern of PBT-MSA complex exhibits sharp diffraction lines in contrast to the pattern of initial PBT powder. The PBT-MSA complex is thus crystalline in nature. Annealing of this complex at 500°C results in its breakdown to give crystalline PBT material.

A similar experiment was carried out on ABPBI powder and results are shown in Figure 8. The x-ray pattern of "virgin" ABPBI powder shows two very broad lines at 3.8A and 8.5A, respectively. In ABPBI-MSA complex, two somewhat sharper lines appear at 4.15A and 10.1A. This increase in lattice spacings results from an incorporation of the solvent into the lattice, causing an expansion of unit cell dimensions. However, unlike the PBT-MSA complex, this complex (ABPBI-MSA) is not crystalline as is evident from line breadths as well as from a paucity of diffraction lines.

The x-ray pattern of ABPBI cast film (Figure 9) is more crystalline than the pattern of ABPBI-MSA complex formed by

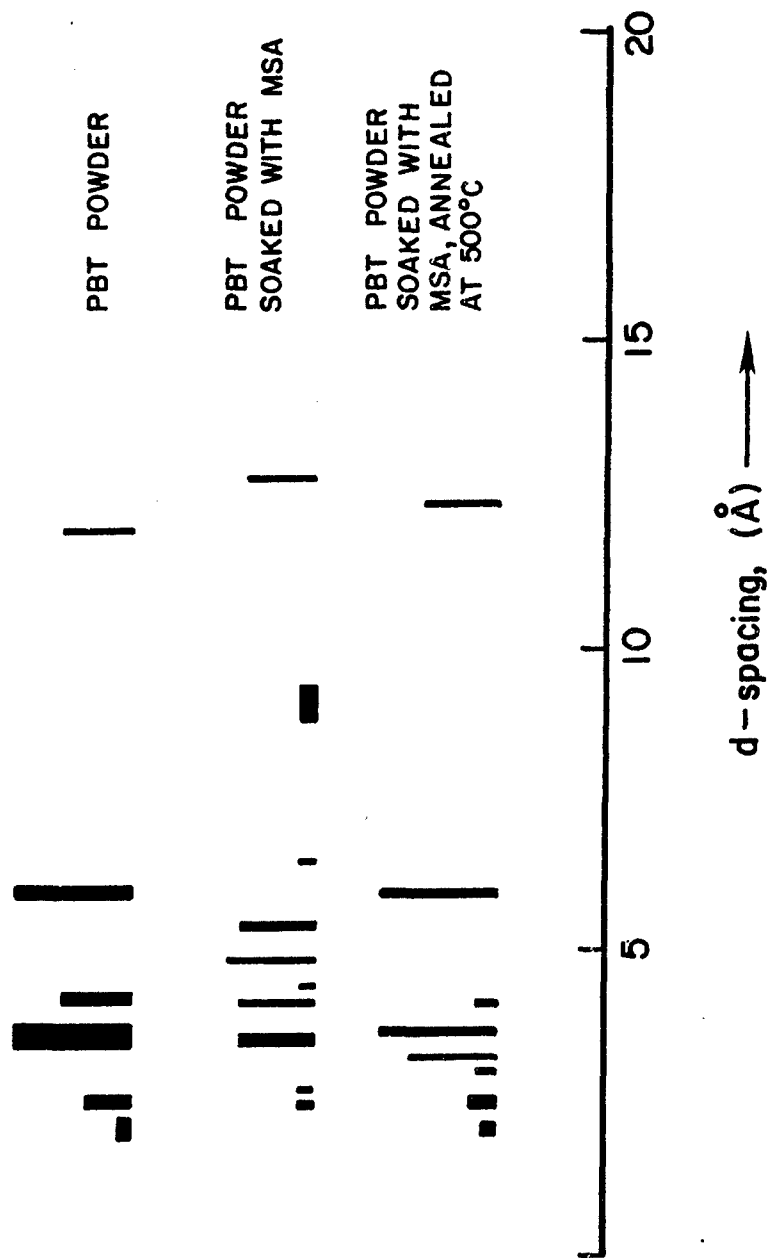


Figure 7. Comparison Between Various Diffraction Data Relating to the Polymer-Solvent Complex Studies with PBT.



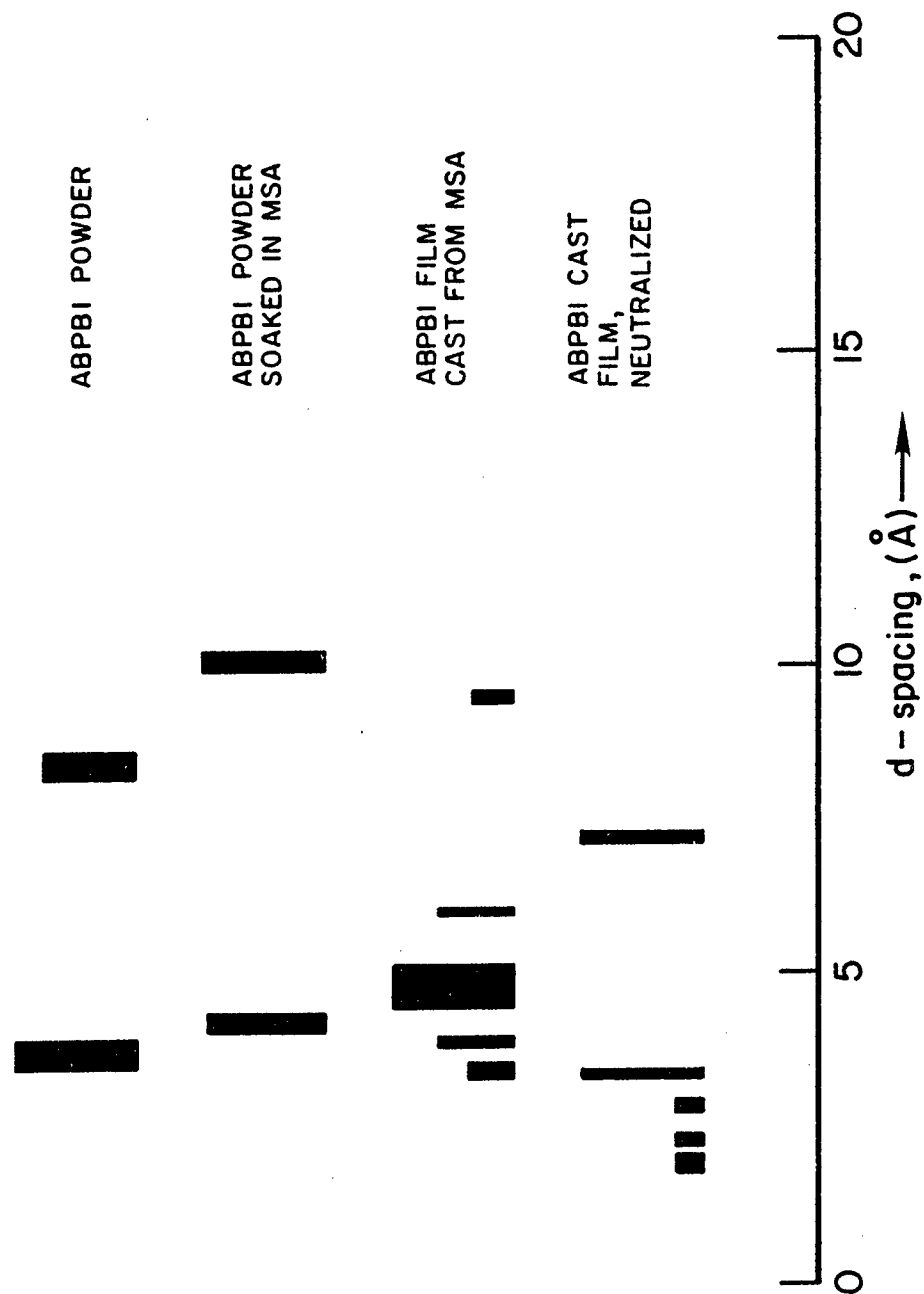
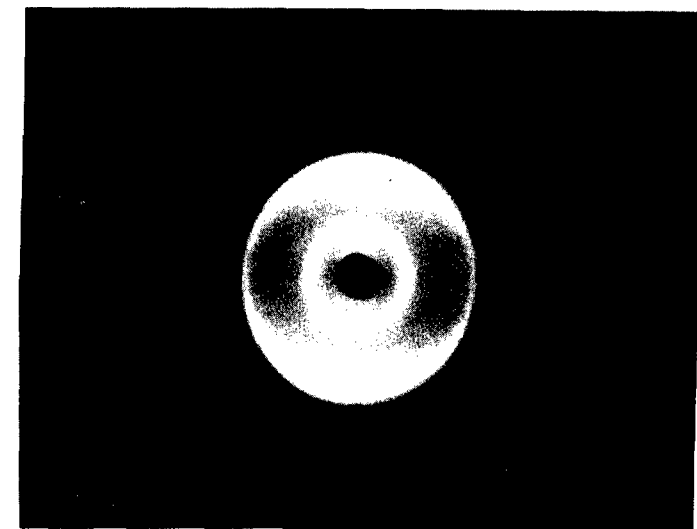


Figure 8. Comparison Between Various Diffraction Data Relating to the Polymer-Solvent Complex Studies with ABPBI.

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a



b

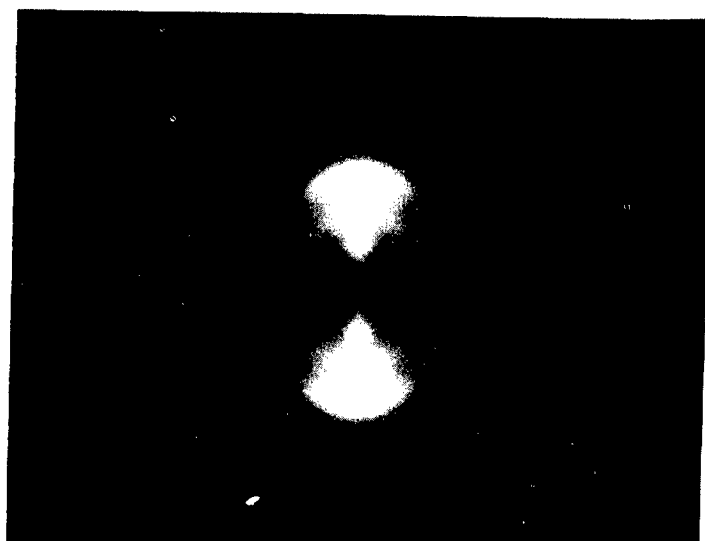
Figure 9. X-ray Photographs of ABPI Film (a) As-cast from MSA (b) Neutralized.

adding MSA to ABPBI powder inside the capillary. Perhaps, the nature of the x-ray pattern of the complex may depend on the amount of solvent retained by the polymer and the process of film casting may have lead to improved crystallinity of the complex. The spacing at 9.5Å in the x-ray pattern of ABPBI cast film can thus be attributed to the complex, while the broad 4.8Å spacing is accounted for by the presence of free MSA. In the x-ray pattern of neutralized cast film, the above-mentioned spacings are not seen. However, the x-ray pattern of neutralized ABPBI cast film is very different from the pattern of ABPBI powder.

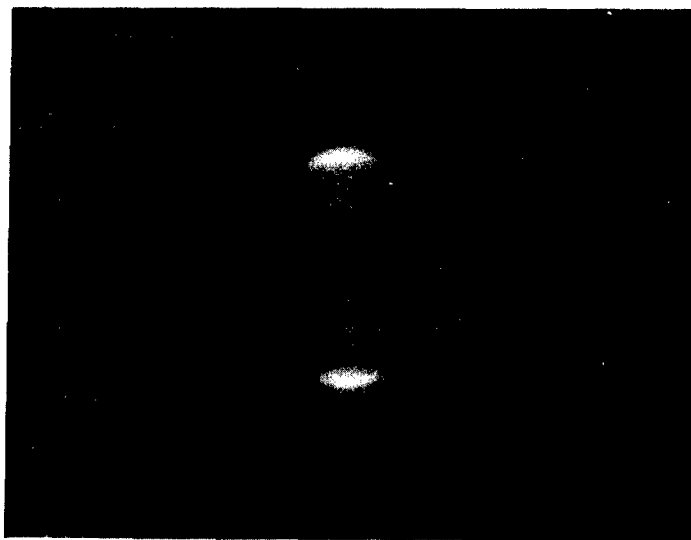
e) Shear Quenched Films

Since the presence of solvent or swelling agent is a prerequisite for stretching polyblend films, it is even easier to stretch a viscous gel of polymer solution itself. A solution of ABPBI and PBT (in MSA) is poured on a microscope glass slide and sheared using another glass slide. The sheared polyblend film is then quenched with water in order to achieve coagulation and precipitation of the material. A film made in this way is designated "hand-sheared quenched film"<sup>3</sup>, abbreviated as HSQF. Hand-sheared quenched films of 80/20, 70/30, 60/40, and 40/60 composition were prepared<sup>3</sup> from solutions of critical concentration ( $C=CR$ ). This critical concentration refers to the concentration of a given polyblend solution above which the phase separation occurs in solution itself, giving rise to isotropic and anisotropic, i.e., a biphasic solution. Below the critical concentration, the solution exists in the isotropic state.

X-ray diagrams of sheared-quenched films of different blend composition are shown in Figure 10 and represented as bar graphs in Figure 11. The x-ray diagrams show the orientation achieved by shearing. The bar graphs of 80/20, 70/30 and 60/40 blends show large d-spacings in 8-10Å range, indicating that they represent diffraction by polymer-solvent complexes which have been oriented by shearing process. Quenching of sheared film with water eliminates most of the free or unbound MSA.



a



b

Figure 10. X-ray Photographs of Sheared, Quenched Polyblend Films  
(a) 80/20 Blend (b) 40/60 Blend.

This is why the peak due to free MSA, which shows up at 4.5 - 4.8A, is absent or very weak (unlike the case with cast films). Pure PBT (or, for that matter, pure ABPBI) does not show any spacing in the 8-10A region.

If, indeed the x-ray diagrams given by sheared-quenched polyblends arise from polymer-solvent complex formation, then neutralizing (or annealing at 500°C) should cause a breakdown of the complex and a corresponding change in x-ray diagram. The effect of neutralizing on the x-ray pattern of 70/30 polyblend is shown at the bottom of Figure 11. Neutralizing causes a disappearance of 9.8A d-spacing (corresponding to the polymer-solvent complex) and appearance of a new spacing at 7.3A, corresponding to the pure ABPBI material.

The x-ray diagrams of neutralized sheared-quenched films become very diffuse, showing a loss in crystallinity and orientation caused by a disorder of macromolecules. The diagrams of annealed, sheared-quenched films show increases in x-ray intensity and a very diffuse background scatter. Neutralization and annealing both lead to a microphase separation in sheared-quenched films. The former causes a decrease in crystallinity while the latter causes an increase over and above the crystallinity of the polymer-solvent complex itself.

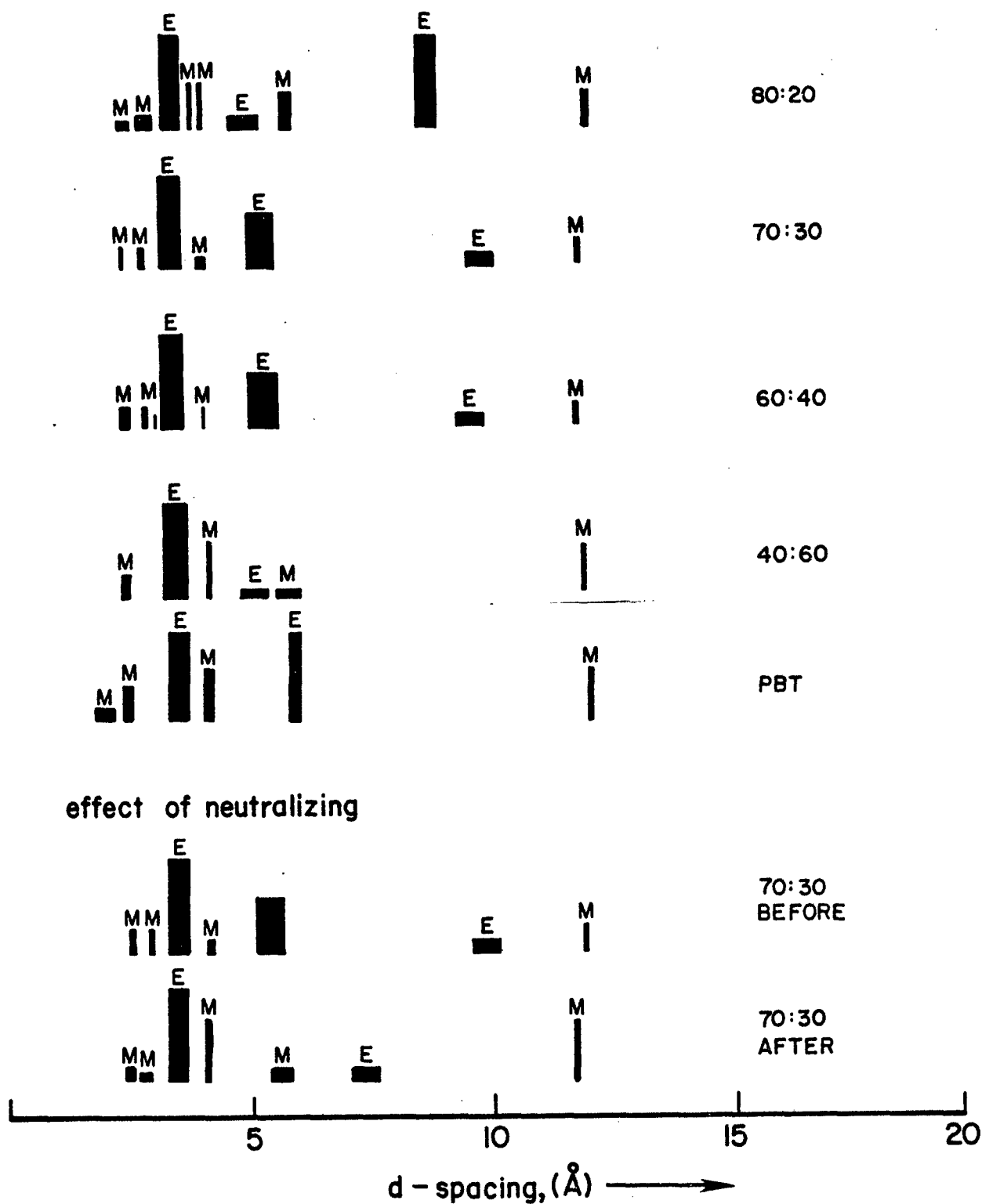


Figure 11. Bar Graph of X-ray Diffraction Results for Sheared Quenched Films of Different Blend Composition (E=Equatorial, M=Meridional).

### SECTION III

#### INFLUENCES AFFECTING MICROSTRUCTURE

##### a) Casting Solvent

Film formation by solvent-casting results in a distinct two-phase blend. The extent of phase separation in cast polyblends obviously depends on the nature of the solvent. Domain structure (i.e., the structure of the dispersed phase) would depend upon the solvation power of the solvent and specifically on the relative solubility differences of constituent polymers in a given solvent. The selectivity in the solvation of two polymers by a given solvent along with independent processing factors, dictates the resultant microstructure of polyblend.

Both ABPBI and PBT are soluble in the following solvents: (1) concentrated sulfuric acid, (2) methane sulfonic acid (MSA), (3) fuming nitric acid (FNA), and (4) polyphosphoric acid (PPA). Films of ABPBI/PBT polyblends were cast with MSA and FNA as casting solvent media. Two different blend compositions were tried in each solvent: 80/20 and 40/60. All cast films were opaque, about 0.5-1.0mm thick and reddish brown in color. For the purpose of comparison, films of pure PBT were also cast in these two solvents (MSA and FNA).

X-ray diffraction bar charts of as-cast 80/20 polyblend, 40/60 polyblend and pure PBT film are shown in Figure 12 for each of the two casting solvents. In all cases, as-cast polyblends show a d-spacing in the range 8-11Å, arising from polymer-solvent association leading to an expanded lattice. The extent of lattice expansion is governed by the size of the solvent molecule. Since MSA has a higher molecular weight than nitric acid, both the 80/20 and the 40/60 polyblends cast with MSA show a higher d-spacing in the 8-11Å range than the corresponding ones cast with FNA (Figure 12). The nature of the x-ray pattern of the as-cast film is not only dependent on the choice of the casting solvent, but also upon the blend composition. The diffraction patterns of as-cast polyblends cannot be reproduced by adding the x-ray patterns of the as-cast films of the constituent polymers.

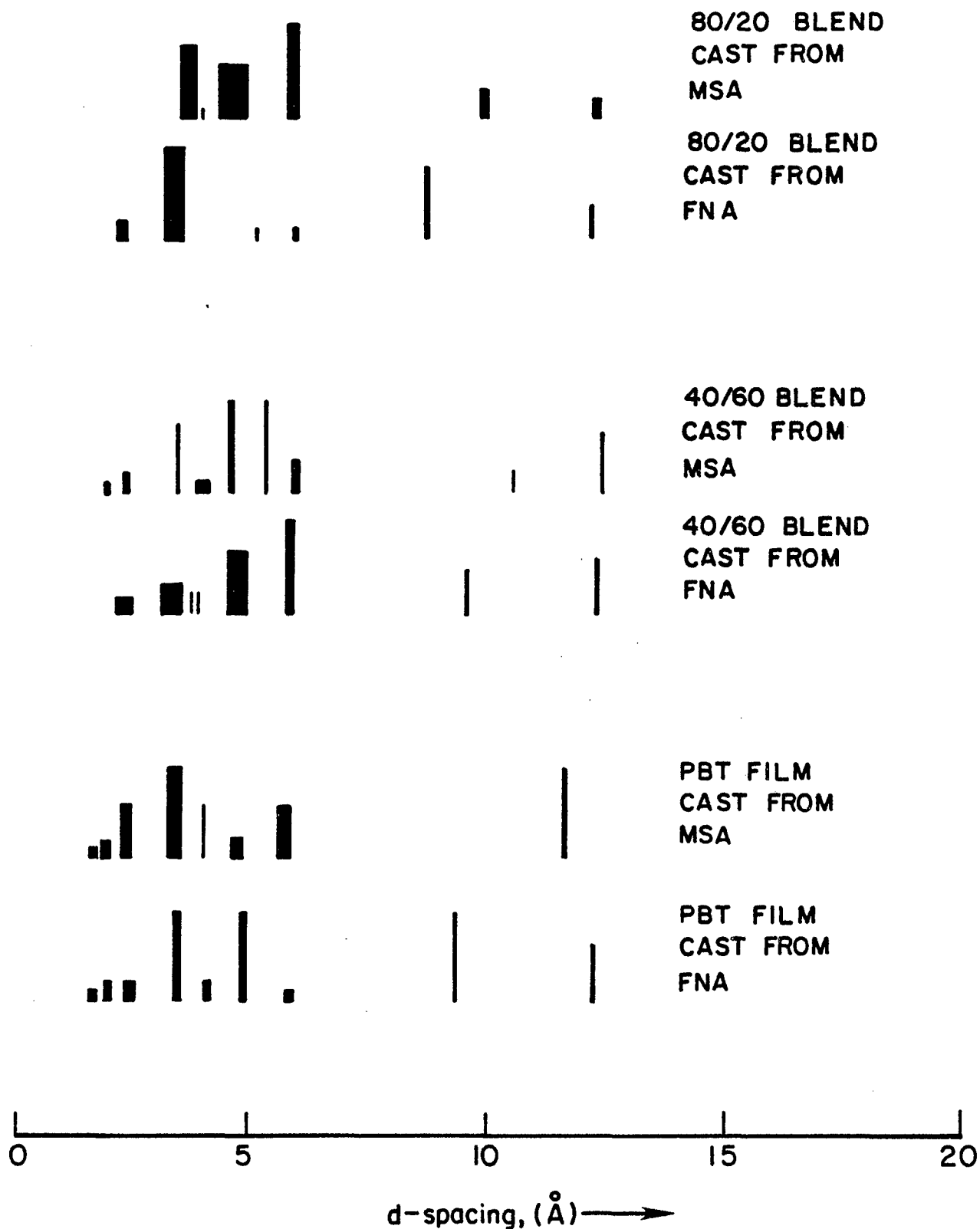


Figure 12. X-ray Diffraction Bar Charts of As-Cast 80/20 Polyblend, 40/60 Polyblend and Prone PBT Film.



b) Neutralizing

Influence of neutralizing on the microstructure of polyblend films has already been discussed in earlier sections of this report dealing with the x-ray studies on 80/20 and 40/60 cast films.

Neutralizing represents a very important step in the processing of polyblend films. Since as-made polyblends (cast or quenched) are in fact polymer-solvent complexes, neutralizing helps in the breakdown of the complex to get rid of the solvent and yield a true polyblend containing only the constituent polymers. As a consequence, the x-ray diagrams of neutralized films are simpler and easy to explain in terms of the diffraction contributions of the constituent polymers.

X-ray bar graphs of neutralized films of cast and quenched polyblends, as well as those of pure polymers are shown in Figures 13 and 14 respectively. The patterns of polyblends shown in Figure 13 can be explained on the basis of additivity of contributions from pure PBT and pure ABPBI components. The polyblends behave as though they are physical mixtures of the two polymers. X-ray data as presented here cannot indicate the level of phase separation (i.e., the size of microphase domains). It is interesting to note from Figure 9 that the bar graphs of 70/30 sheared-quenched film and 80/20 MSA-cast film show contributions from both ABPBI and PBT. On the other hand, the bar graph of 40/60 polyblend (MSA cast) shows contribution from PBT component only, meaning thereby that associated ABPBI exists in an amorphous form.

Figure 13 shows x-ray data on neutralized films which were cast from FNA. These results also indicate that both 80/20 and 40/60 polyblends represent bicomponent two-phase mixtures of PBT and ABPBI.

c) High Temperature Annealing

Annealing of polyblends was done at 500°C for 5 minutes under vacuum.

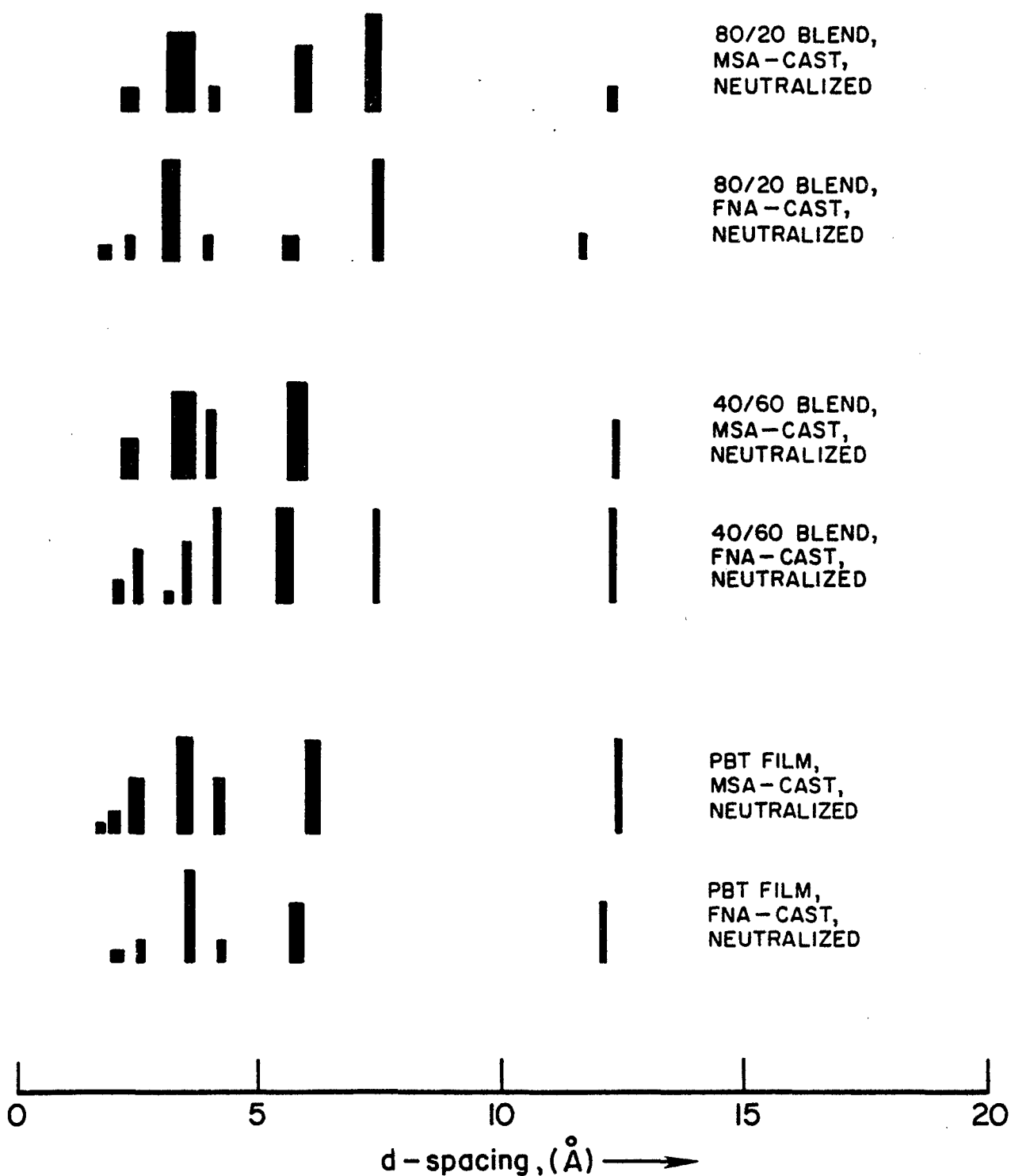


Figure 13. X-ray Diffraction Bar Graphs of Neutralized Films of Cast and Quenched Polyblends.

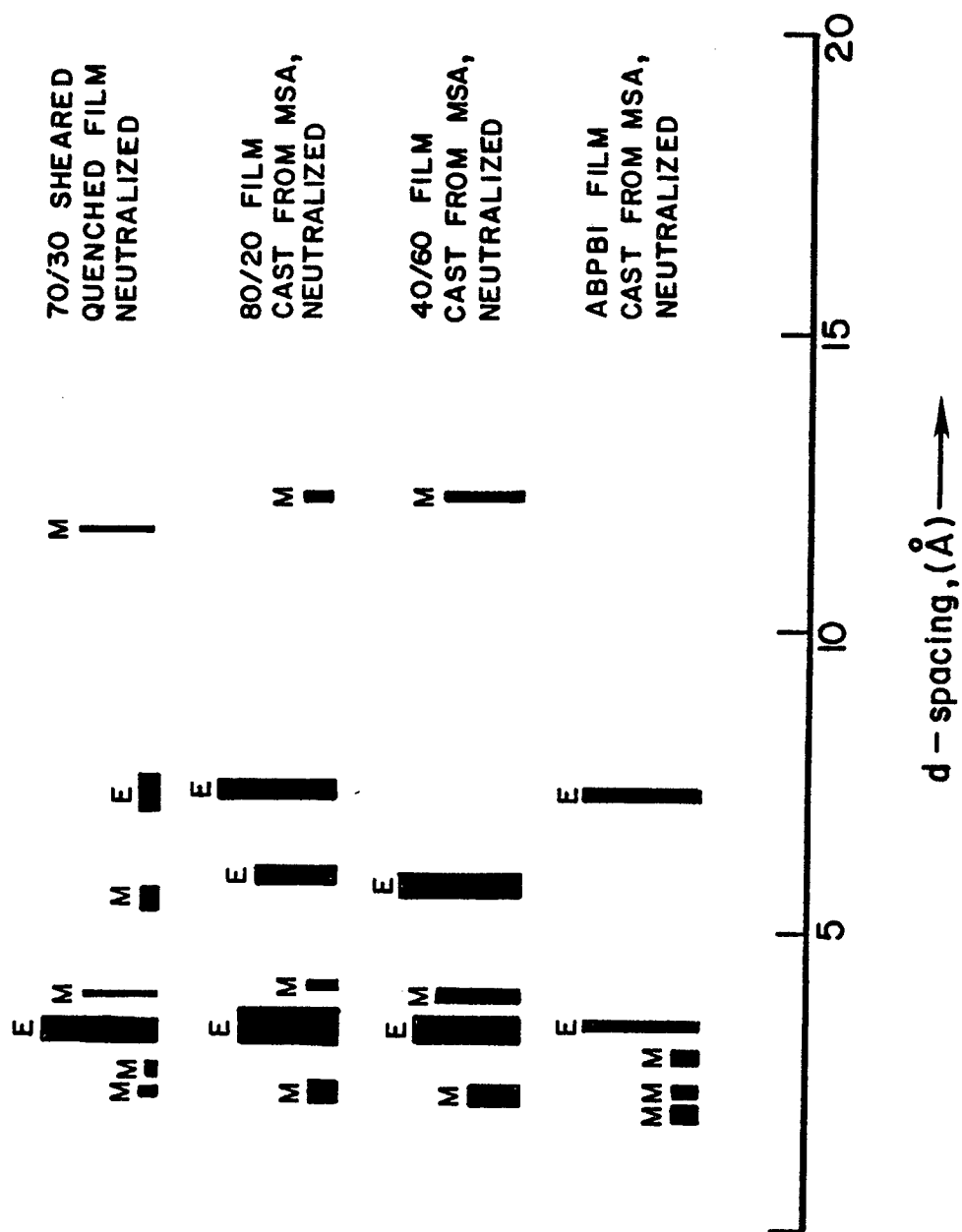


Figure 14. Bar Graphs Representing X-ray Diffraction Results of Cast and Sheared Films (E=Equatorial, M=Meridional).

In most cases, x-ray bar graphs of annealed polyblends represent diffraction by the crystalline aggregates of rod-like PBT macromolecules (Figure 15). This happens to be true, regardless of blend composition, the type of solvent (MSA or FNA) or the nature of processing method (casting or shear-quenching). This is attributed to a phase-separation phenomenon which results from a decrease in polymer-polymer miscibility at high temperatures ( $\sim 500^{\circ}\text{C}$ ) due to increase in crystallinity of the rod-like constituent (PBT). During this phase-separation process, molecules of ABPBI are forced apart by the aggregating rod-like molecules, and coil-up in amorphous state. This appears to be the only possible explanation of the observation that x-ray bar graphs of annealed polyblends show no contribution from ABPBI. The patterns of annealed polyblends (Figures 16, 17, 18) are easy to interpret because they show high crystallinity, have no influence of solvent and show no contribution from ABPBI.

X-ray bar graphs of annealed 40/60 polyblend are shown in Figure 19 as a function of annealing temperature.

d) Solvent-Stretching

In addition to crystallinity, crystallite orientation is a very important morphological variable which influences the mechanical properties of polyblends. As-processed polyblends of ABPBI and PBT (prepared by casting or quenching) contain appreciable amounts of MSA in the form of crystalline polymer-solvent complexes. In addition, there is some unbound MSA present in the cast polyblend films. This retained solvent may act as a plasticizer and help in stretching the films for the purpose of improving the crystallite orientation. It is known that methanol acts as a swelling medium for as-processed films and the application of methanol promotes a stretching of the films (Figure 20). Crystallite orientation can be improved considerably in the 80/20 polyblend (cast from MSA), first by allowing it to swell in methanol for 8 to 10 hours and then stretching it. Films can be stretched to 200% - 300% above the initial length by this technique. However, when this technique

# EFFECT OF ANNEALING ( 500°C, 5 MIN.)

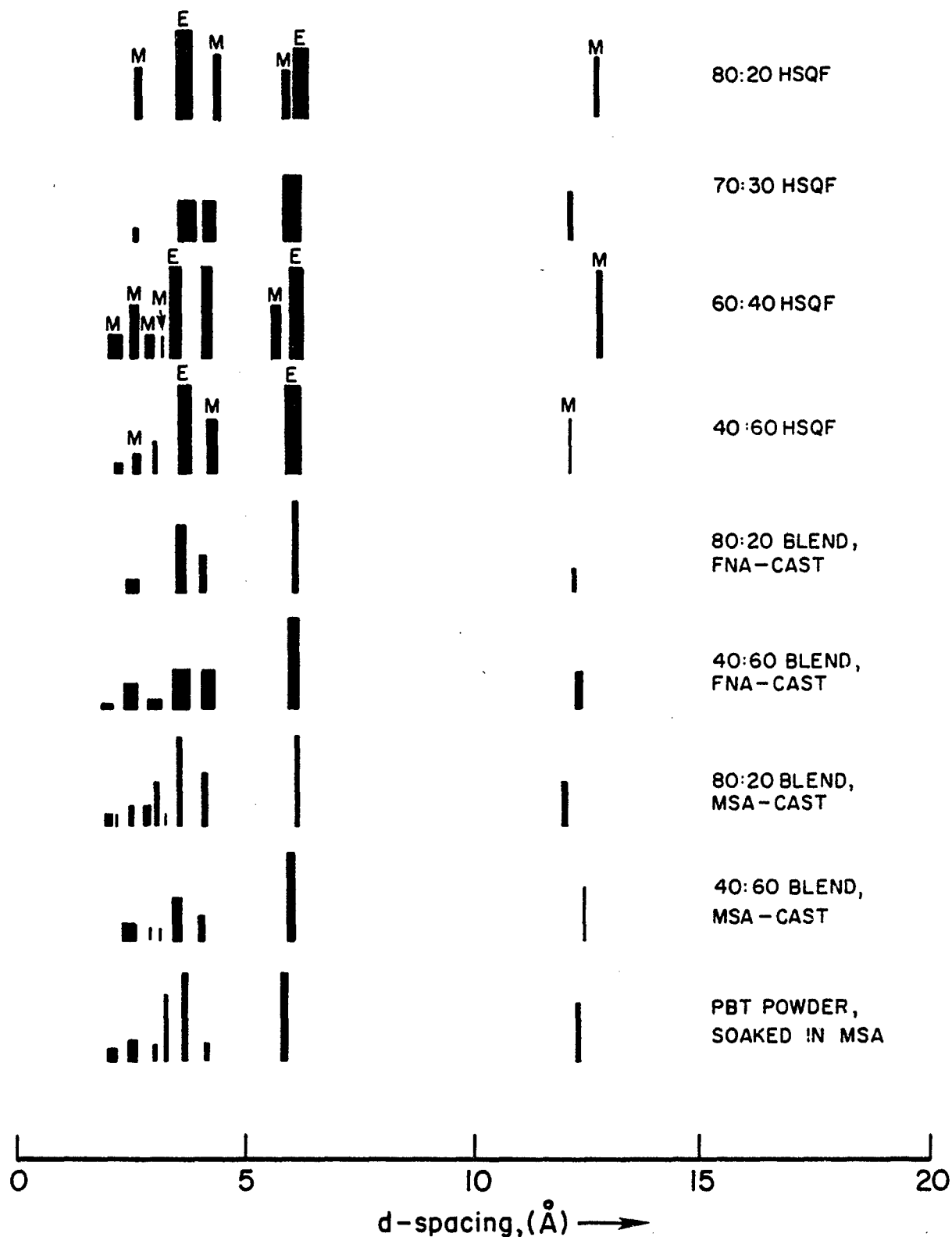
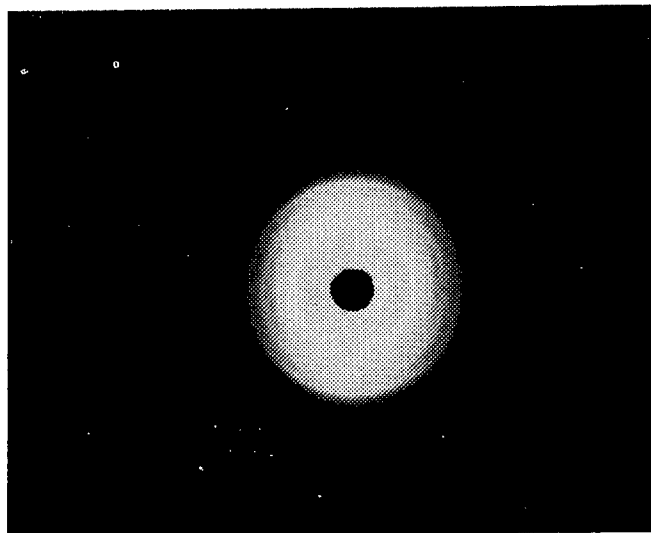
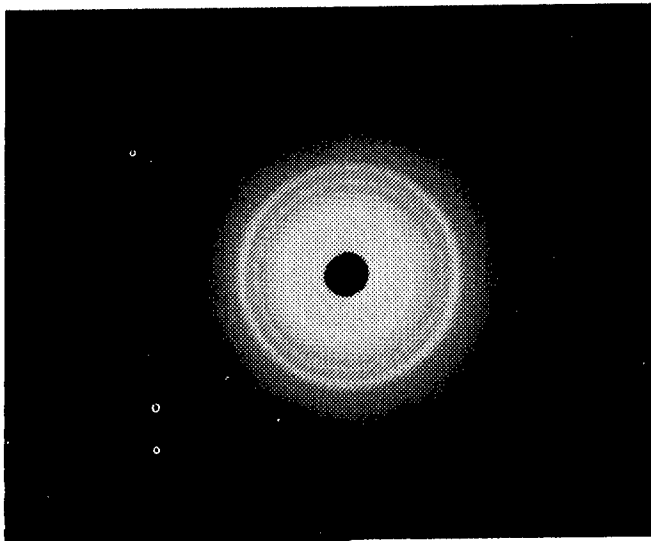


Figure 15. X-ray Bar Graphs of Annealed (500°C, 5 min) Polyblends.



80/20 MSA-CAST, ANNEALED AT  
500°C FOR 5 MIN IN VACUUM

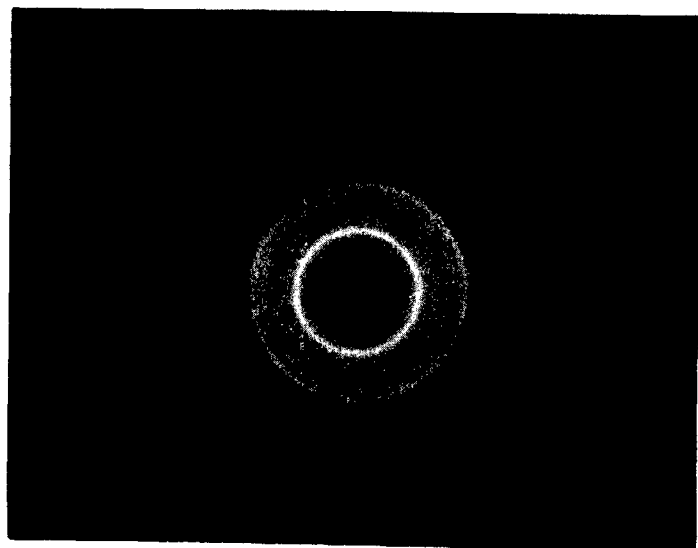
a



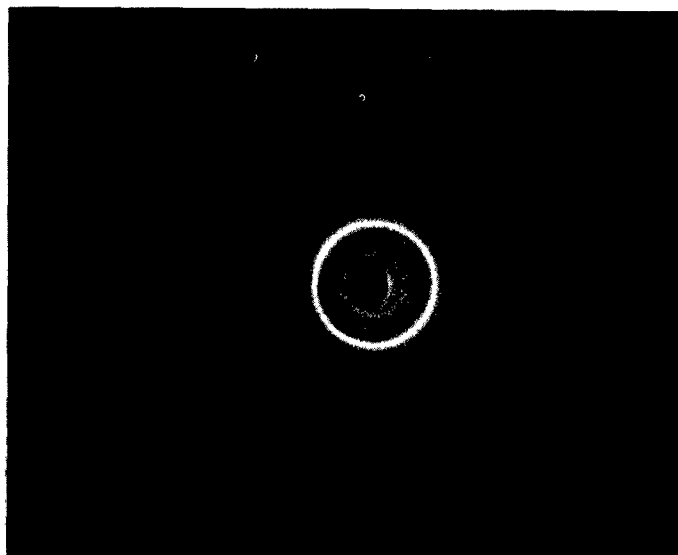
40/60 MSA-CAST, ANNEALED AT  
500°C FOR 5 MIN IN VACUUM

b

Figure 16. X-ray Photographs of MSA-cast Polyblend Films, Annealed at 500 C for 5 Min in Vacuum (a) 80/20 Blend (b) 40/60 Blend.

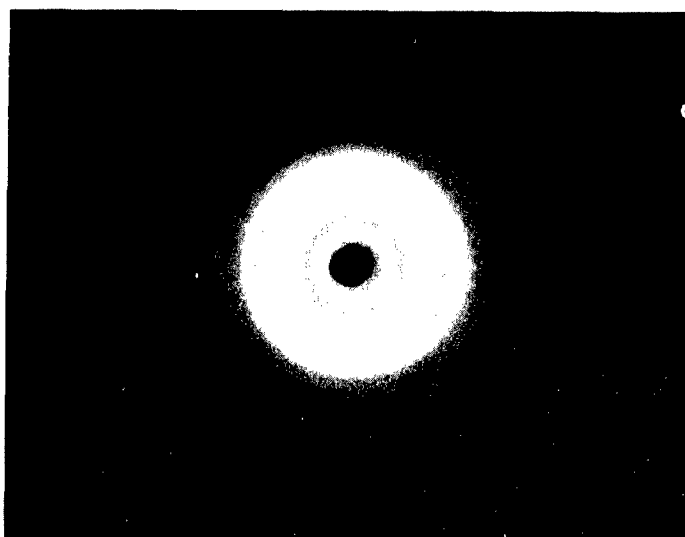


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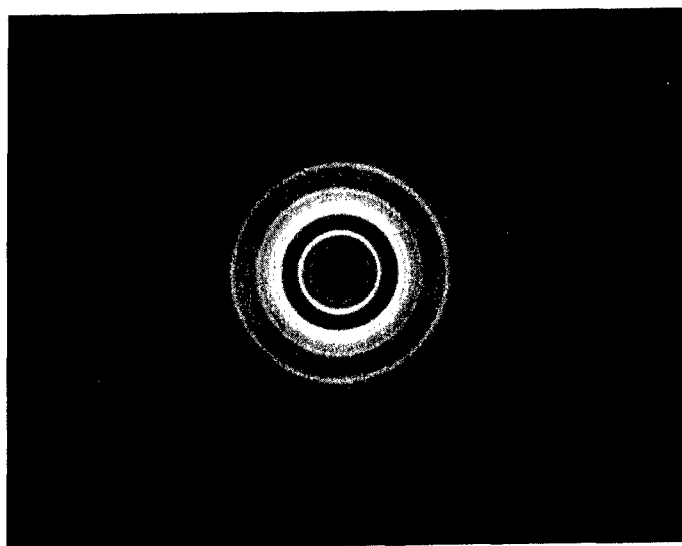


b

Figure 17. X-ray Photographs of FNA-cast Polyblend Films, Annealed at 500 C for 5 Min in Vacuum (a) 80/20 Blend (b) 40/60 Blend.



a



b

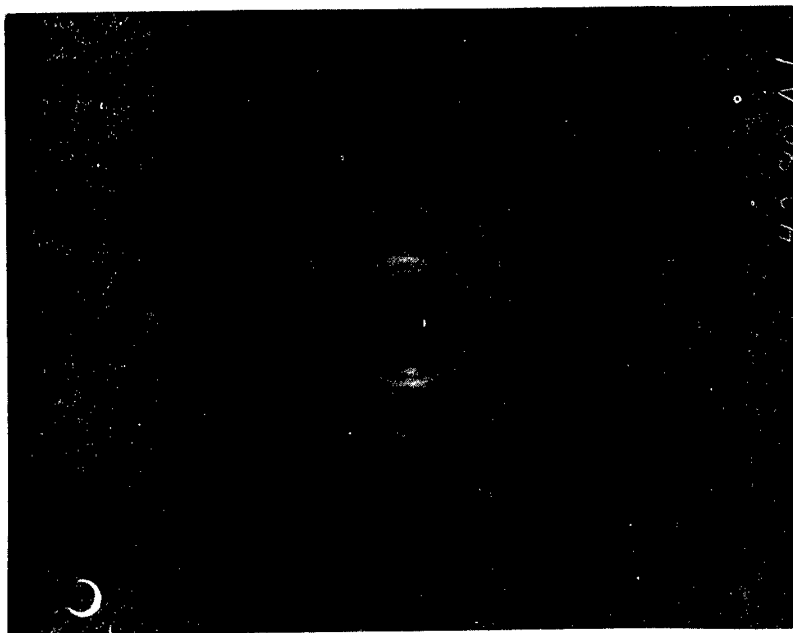
Figure 18. X-ray Photographs of MSA-cast 40/60 Polyblend Film (a) Annealed at 400 C (b) Pressure-Annealed at 10000 lb., 425 C.

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a



b

Figure 20. X-ray Photographs of (a) 80/20 Polyblend Film, Quenched From 4.24% Solution and Solvent-Stretched to 16.5% with Methanol (b) 40/60 MSA-cast Polyblend Film, Stretched to 100% with  $\text{HNO}_3$ , Neutralized.

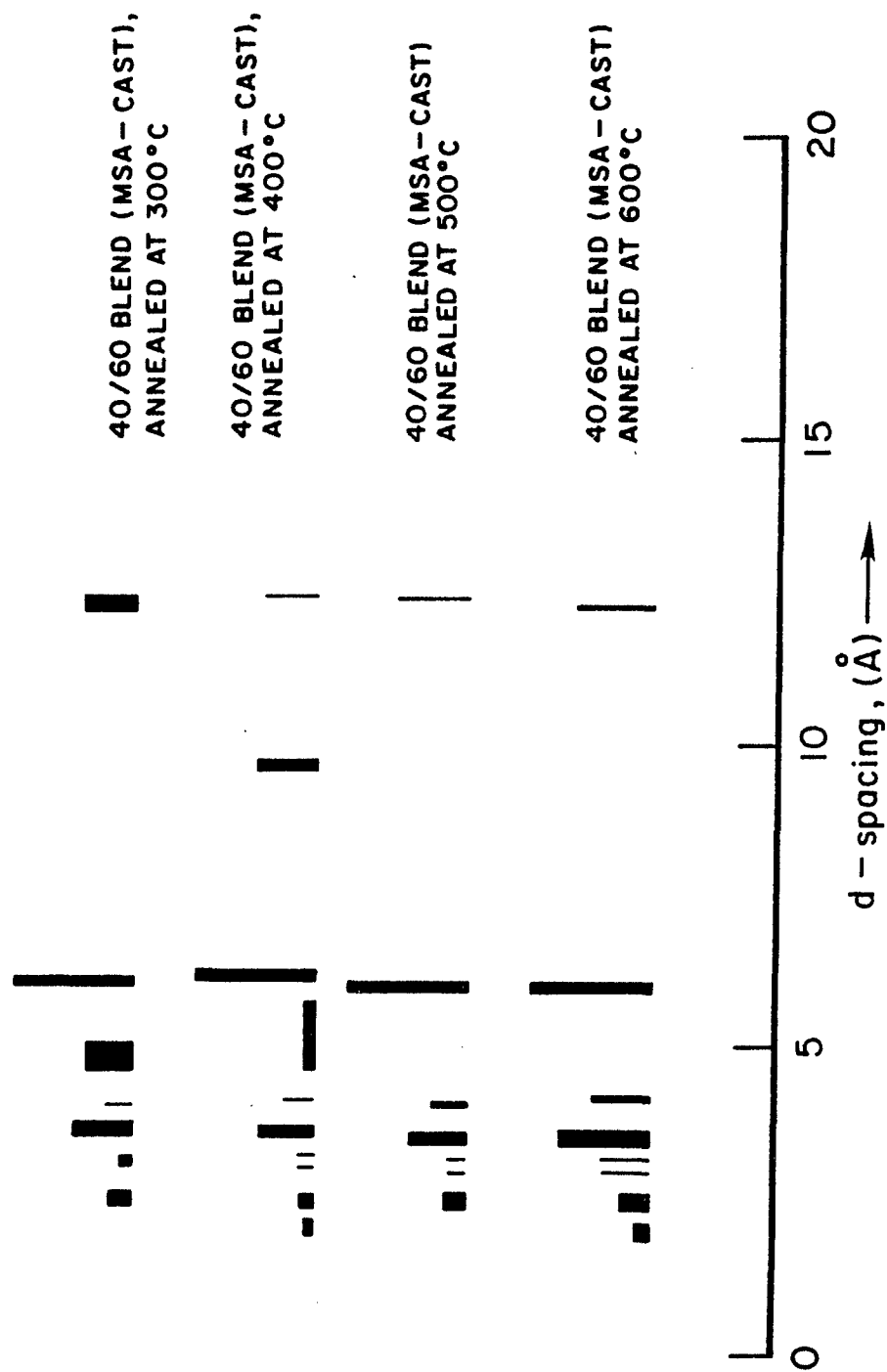


Figure 19. X-ray Bar Graphs of Annealed 40/60 Polyblend.

is applied to the 40/60 blend, a stretch of only about 15% is attainable. This indicates that methanol is able to plasticize only the ABPBI component of the polyblend and becomes ineffective as a swelling medium in polyblends containing high percentage of rods.

Attempts were therefore made to swell and stretch the polyblends using different acids as swelling agents. During these efforts, it was discovered that trifluoroacetic acid (TFAA) was an excellent swelling agent which permitted stretch levels of 200% to 300% even in rod-rich polyblends (Figure 21). In 90/10 or 80/20 polyblends, one had to be careful in allowing only small amounts of TFAA to film surface before stretching otherwise the film would dissolve and disintegrate. Control experiments were carried out on the virgin polymers using TFAA and it was discovered that TFAA was an excellent solvent for ABPBI. It formed a swollen gel with the ABPBI polymer. On the other hand, TFAA did not swell PBT but caused a color change from yellow to orange.

Since annealing helps in eliminating the solvent as well as improves the crystallinity, stretched polyblends were annealed at 400°C for five minutes (Figure 22). This combination of stretching and annealing improved the x-ray diagrams of polyblends considerably.

e) High Pressure Annealing

The role of annealing to improve the polyblend crystallinity has been discussed earlier in this report. However, annealing becomes an even more powerful tool when carried out simultaneously with the application of pressure (pressure-molding and annealing). Subjecting a solvent containing as-made polyblend film to the combined influence of pressure-molding and annealing results in a further increase of crystallinity than possible with annealing only. This is not surprising because stiff aromatic polymers do require special processing techniques in view of their thermal resistance and glassy character.

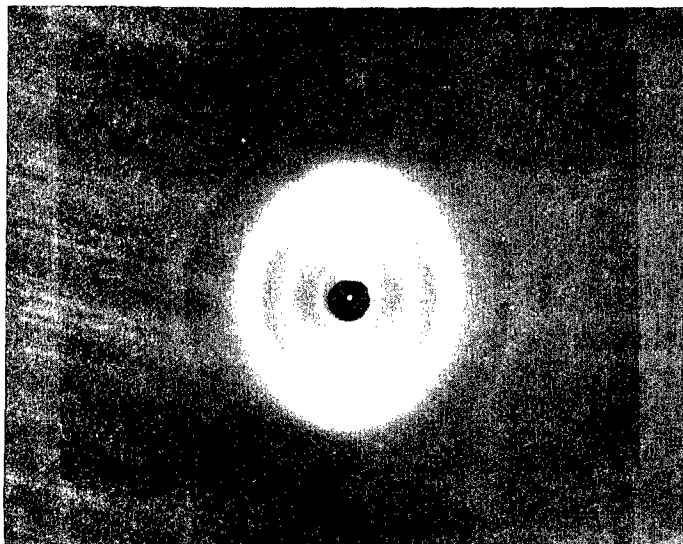
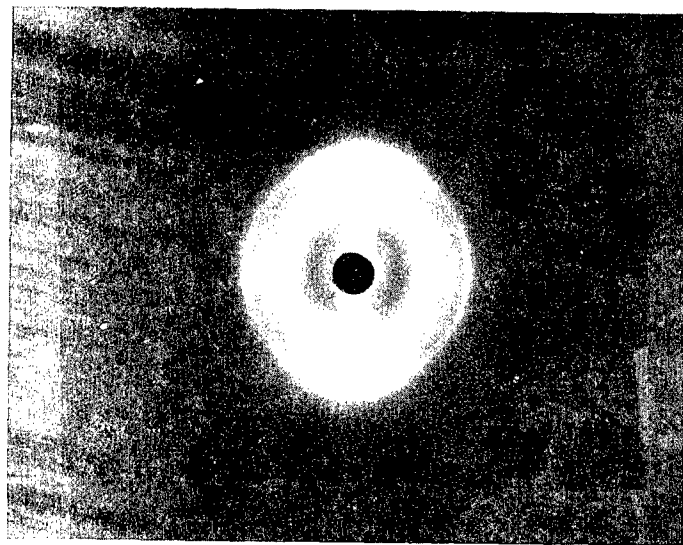
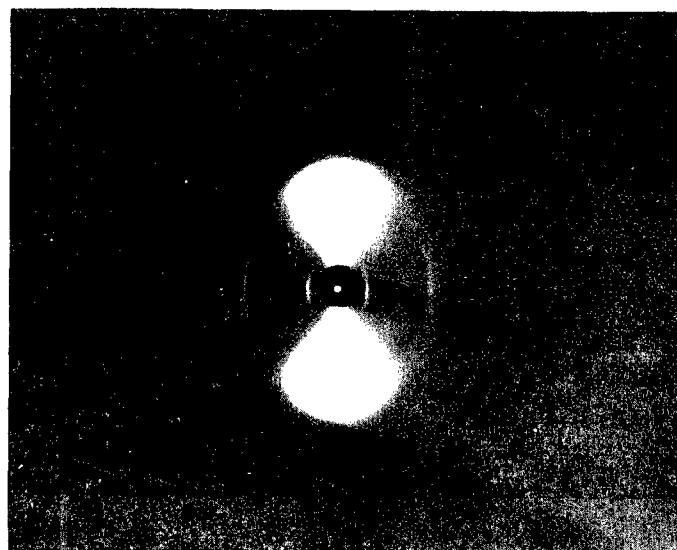


Figure 21. X-ray Photographs of (a) 90/10 MSA-cast Polyblend Film, Stretched to 200% with TFAA (b) 40/60 MSA-cast Polyblend Film, Stretched to 150% with TFAA and Neutralized.



a



b

Figure 22. X-ray Photographs of (a) 60/40 Sheared-Quenched Film, C=Cr, Annealed at 500 C for 5 Min (b) 40/60 MSA-cast Polyblend Film, Stretched to 160% with TFAA, Annealed at 400 C.

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Application of pressure as a tool for the improvement of crystallinity in aromatic polymers is well-known. For instance, polybenzimidazole polymer (PBI) is amorphous, but pressure treatment with phenol at 290-305°C for two hours causes it to crystallize. A marked increase in crystallinity of poly(p-phenylene) takes place as a result of pressing the powder, increasing the molding temperature, and subsequent annealing at 400°C for 24 hours. Thus, pressure-molding and annealing represents a promising approach for improving the crystallinity of ABPBI/PBT polyblends.

A 40/60 MSA-cast polyblend film was selected for pressure-molding and annealing. Prior to the experiment, the cast film was squeezed between a folded blotting paper, to remove free MSA from its surface. The film was then sandwiched between several layers of aluminum foil and folded on all sides in order to make the sandwich air-tight. Care was taken to keep the cast film flat inside the sandwich. This aluminum foil-cast film sandwich was then placed between two very flat stainless steel plates which could be used for the application of heat and pressure. The steel plates were heated to 425°C and a maximum load of 1000 lb was applied for 30 minutes. After this treatment, the sandwich was removed and the cast film taken out.

The x-ray diffraction of this pressure-annealed 40/60 polyblend film is shown in Figure 4. This diffraction pattern shows the highest crystallinity ever achieved in an ABPBI/PBT polyblend! The x-ray pattern is notable not only for the larger number of diffraction lines but also for their amazing sharpness. Bar graph of this x-ray pattern is compared with the bar graph of the same polyblend annealed at 400°C in Figure 23. It should be brought to attention here that the x-ray pattern of the pressure-annealed film represents diffraction from polymer-solvent complex which has undergone an enormous increase in crystallinity. Pressure-annealing of the 40/60 polyblend at the higher temperature of 500°C (at which the solvent dissociates itself from the polyblend) was not attempted due to the presence

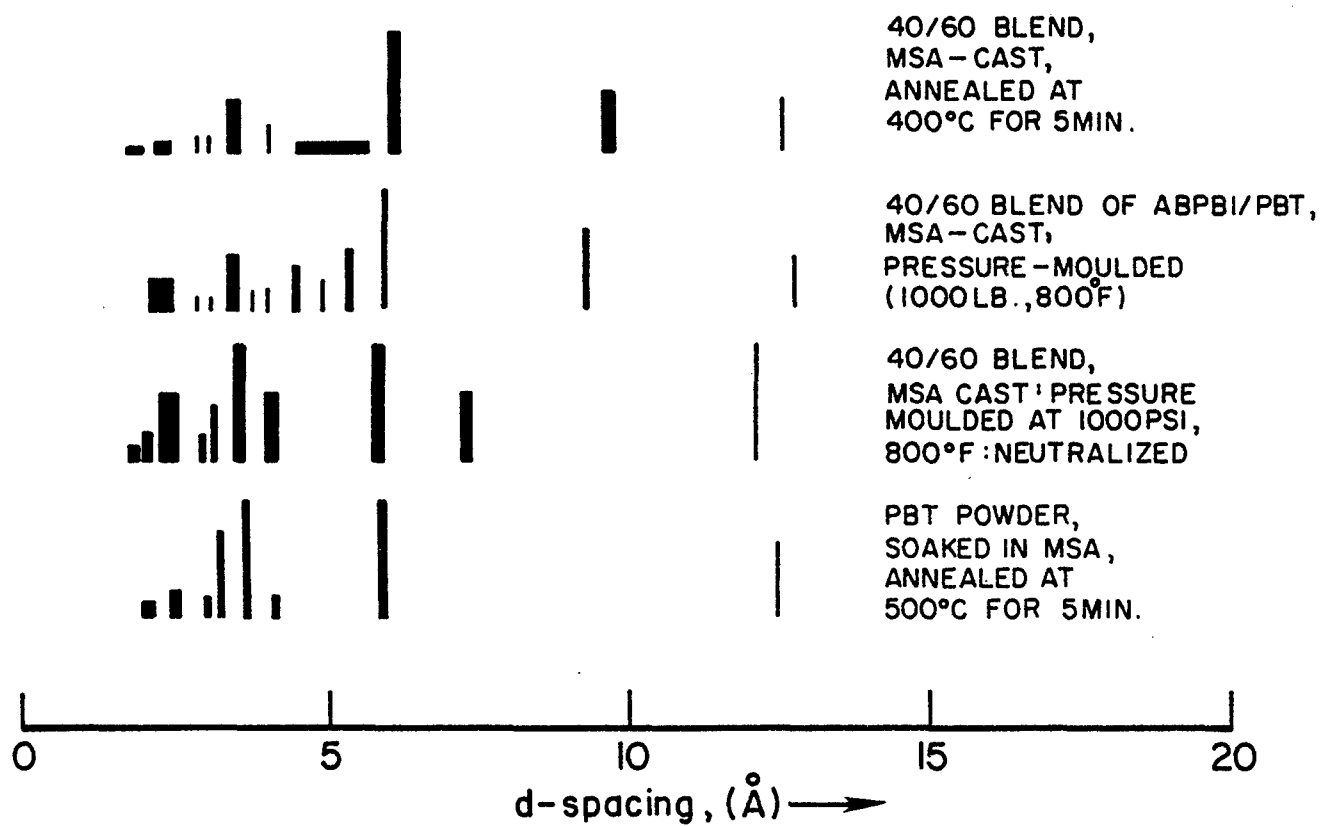


Figure 23. Bar Graph of 40/60 Blend Annealed at 400°C and 1000 psi Pressure.

of air during this process, which may cause a severe degradation of the polymer(s).

This pressure-annealed film was subsequently neutralized (with  $\text{NH}_4\text{OH}$ ) in order to break the polymer-solvent complex. The x-ray pattern of the neutralized pressure-annealed film is shown in Figure 23. The neutralized film retains all the improvement in crystallinity obtained by pressure-annealing. This technique therefore represents a new and novel way of processing polyblends with a goal of improving their crystallinity in order to attain better mechanical properties.

f) DMSO Past Treatment

It was noticed that when a piece of cast-film is immersed in dimethyl sulfoxide (DMSO), it undergoes a color change from reddish brown to yellow. No shrinkage of film was observed. Color changes were observed for polyblends cast with MSA as well as those cast with FNA. X-ray diffraction studies of DMSO treated polyblends were undertaken in order to investigate the relationship between color change on one hand the microstructural change on the other.

Figure 24 shows a comparison of x-ray bar graphs of various polyblends, obtained with and without the application of DMSO. In every case, significant changes in the intensity and position of diffraction lines are observed as a consequence of DMSO treatment (Figure 25). Thus, it may be possible for DMSO molecules to penetrate the molecular lattice of cast film (i.e., the lattice of polymer-solvent complex) and become a part of it. The other (more plausible) possibility is that DMSO may be able to bond with solvent (MSA or FNA) molecules by complexing with them and extract a part of solvent associated with molecular lattice. Both these mechanisms would lead to changes in the position and intensity of lines observed in bar graphs (Figure 24).

DMSO treatment was also carried out on pure PBT and also on neutralized polyblend samples. No changes in x-ray patterns were found as a result of this treatment. Thus, DMSO is effective



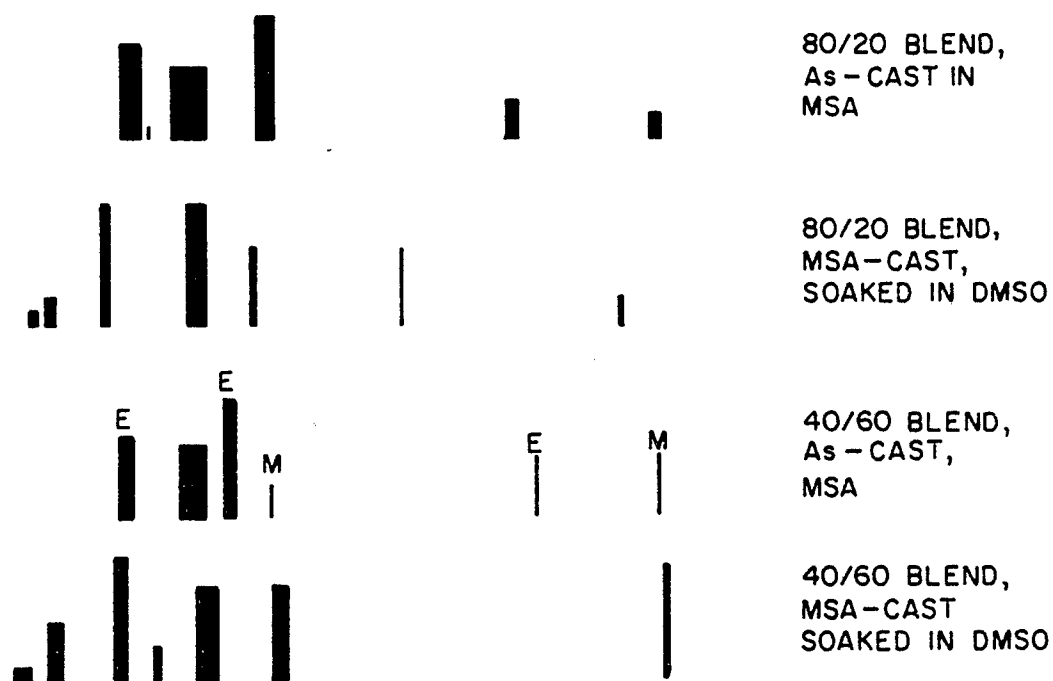
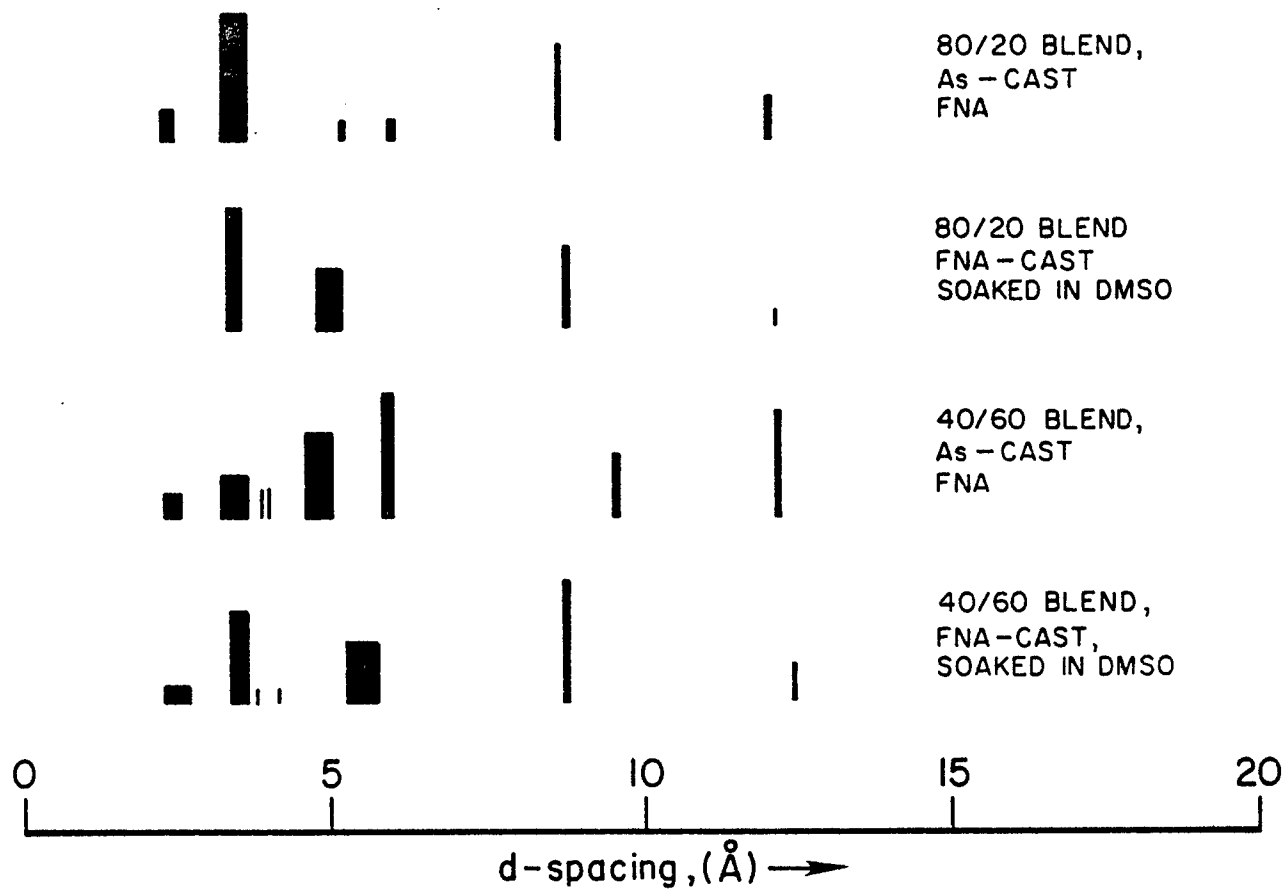


Figure 24. A Comparison of X-ray Bar Graphs of Various Polyblends, With and Without Application of DMSO.

in causing microstructural changes within the polyblend only in the presence of another solvent (MSA or FNA). It thus acts as a co-solvent.

## SECTION IV

### CONCLUSION

1. X-ray diffraction studies on ABPBI/PBT polyblends conclusively suggest that there is no polymer-polymer miscibility at the molecular level and give evidence of a phase-separation effect<sup>7</sup>. X-ray diffraction patterns of cast films and shear-quenched films simply represent the sums of contributions of diffraction by the individual constituent polymers. The expanded size of unit cell in both cast and shear quenched films is due to an incorporation of solvent molecules in the lattice. This judgement has been arrived at by carrying out control experiments on the "virgin" polymers - ABPBI and PBT. In these control experiments, x-ray patterns were obtained for:

- a) the pure polymer (ABPBI or PBT)
- b) polymer and MSA
- c) sample in (b), heated until the elimination of MSA.

These x-ray patterns showed that both PBT and ABPBI get involved in polymer-solvent complex formation. The polymer-solvent complex formed by PBT is of much higher crystallinity than the one formed by ABPBI.

2. The size of the unit cell of the polymer-solvent complex is governed by the size of the solvent molecule.

3. A decomposition of the polymer-solvent complexes found in as-made films (cast or sheared-quenched) by neutralizing or by annealing at 500°C invariably leads to polyblends exhibiting a two-phase morphology.

4. The nature of the x-ray diagram of the polymer - solvent complex is controlled by blend composition, amount and type of solvent present, and the method of processing the film.

5. Good orientation seen in solvent-stretched polyblends and sheared-quenched polyblends indicates that polymer-solvent complex can be oriented.

6. Annealing of polyblends improved the crystalline order.

7. Pressure-annealing sequence gives the highest attainable crystallinity in polyblends.

8. Solvent-Stretching of as-cast films followed by annealing can give films having the benefits of high crystallinity as well as improved orientation.

9. DMSO is capable of modifying the microstructure of as-cast polyblend films.

10. Cast polyblend films of various blend composition can be stretched to 200 to 300% beyond original length with the help of TFAA, which acts as a swelling agent/plasticizer.

In light of these findings we recommend that future research consider the following approaches:

1. Prepare polyblend films using polyphosphoric acid as a solvent for ABPBI and PBT.

2. Investigate the effects of neutralizing and/or annealing on the microstructure of DMSO-treated polyblend films.

3. Evaluate the mechanical properties of oriented polyblend films crystallized by pressure-annealing (preferably done in vacuo).

4. FTIR studies on the polymer-solvent complex.

5. FTIR studies of incompatibility in ABPBI/PBT polyblends.

6. Studying the feasibility of finding a suitable matrix polymer (other than ABPBI) which would form EDA (electron-donor acceptor) complexes with PBT. This would lead to polymer reinforcement at the molecular level.

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APPENDIX 1  
ABBREVIATIONS USED  
IN THIS REPORT

Neutralizing	Treating with aqueous $\text{NH}_4\text{OH}$ , washing and drying
XRD	X-ray Diffraction
MSA	Methane Sulfonic Acid
FNA	Fuming Nitric Acid
DMSO	Dimethyl Sulfoxide
PBT	Poly (p-phenylene benzobisthiazole)
ABPBI	Poly - 2,5 (6) benzimidazole
CSA	Chloro-Sulfonic Acid
MSA-cast film	Film cast from a solvent mixture containing 97.5% MSA and 2.5% CSA
TFAA	Trifluoroacetic Acid

NOMENCLATURE

Referring to blend composition, the first percentage refers to the concentration of the coil-type matrix material (ABPBI), while the second figure represents the concentration of reinforcing rod-type polymer (PBT). Thus, a 40/60 polyblend would represent a film made by mixing 40% ABPBI and 60% PBT.